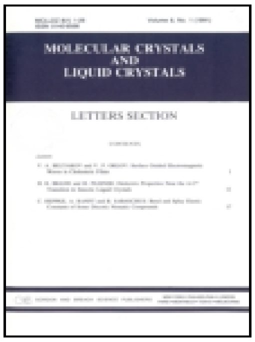

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Synthesis and Study of Molecular Structure and Its Relation to Liquid Crystal Behavior in a Novel Azoester Series

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A novel liquid crystal (LC) homologous series of 12 azoesters was synthesized and evaluated, and nine members of the series exhibited enantiotropically or monotropically nematogenic LC behavior. Smectogenic character is totally absent. The methoxy, tetradecyloxy, and hexadecyloxy homologues are non-liquid crystals (NLC). Textures of nematic phase are threaded, or schlieren. The solid–isotropic/nematic and N-I or vice versa transition curves behave in normal manner. The N-I transition curve exhibits an odd-even effect. The average thermal stability for nematic is 113.25°C. Mesomorphic phase length ranges from 21 to 35°C. The textures of nematic mesophase and transition temperatures were determined by an optical polarizing microscope equipped with a heating stage. Analytical and spectral data confirm the molecular structures of homologues. The LC behavior of the present novel series is compared with a structurally similar known series. The present series is predominantly nematogenic with the absence of smectic property, and is of a middle-ordered melting type.

Keywords Azoester; liquid crystals; monotropy; smectic; nematic

Introduction

Since the report [1] of a novel physical state of matter intermediate between crystalline solid and isotropic liquid, all research groups of various branches of science and technology have shared their keen interest to exploit the liquid crystalline (LC) state with different aims and objects because of its dual characteristics of flow as an ordered liquid and an ability to show optical behavior [2–6]. Chemists have designed and synthesized novel LC compounds by varying the geometrical shape, size, aromaticity, terminal end group or groups, central and/or lateral groups, and their position of substitution as ortho, meta, and para, and studied or evaluated their effects on LC behavior and molecular structure [7–10] as a consequence of molecular rigidity and/or flexibility. In continuation of the same, the present investigation is planned to synthesize a novel homologous series of LC compounds with azo (—N=N—) linkages, which are thermally very stable and undergo a trans-cis isomerism in presence of UV light, and are useful for electrooptical devices and photochromism [11, 12]. The present investigation will cover only the synthesis of

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Table 1. Elemental analysis for propyloxy, hexyloxy, decyloxy, and tetradecyloxy derivatives

		% Elements found (% calculated)		
Sr. No.	Molecular formula	C	H	N
1.	$C_{22}H_{17}N_3O_5Cl_2$	55.79(55.70)	3.45(3.59)	8.77(8.86)
2.	$C_{25}H_{23}N_3O_5Cl_2$	58.25(58.14)	4.49(4.46)	8.23(8.14)
3.	$C_{29}H_{31}N_3O_5Cl_2$	60.78(60.84)	5.49(5.42)	7.26(7.34)
4.	$C_{33}H_{39}N_3O_5Cl_2$	63.17(63.06)	6.29(6.21)	6.76(6.69)

novel azoester compounds with three phenyl rings, two laterally substituted –Cl groups at the middle phenyl ring, and left and right terminal end groups of –OR and $–NO_2$. The novel compounds were characterized by elemental analysis, spectral data, and LC behavior by an optical polarizing microscope equipped with a heating stage. Their LC behavior was evaluated in terms of molecular rigidity and flexibility [13–16]. Other scientific and technological investigations, including applications, will be studied by other groups of researchers.

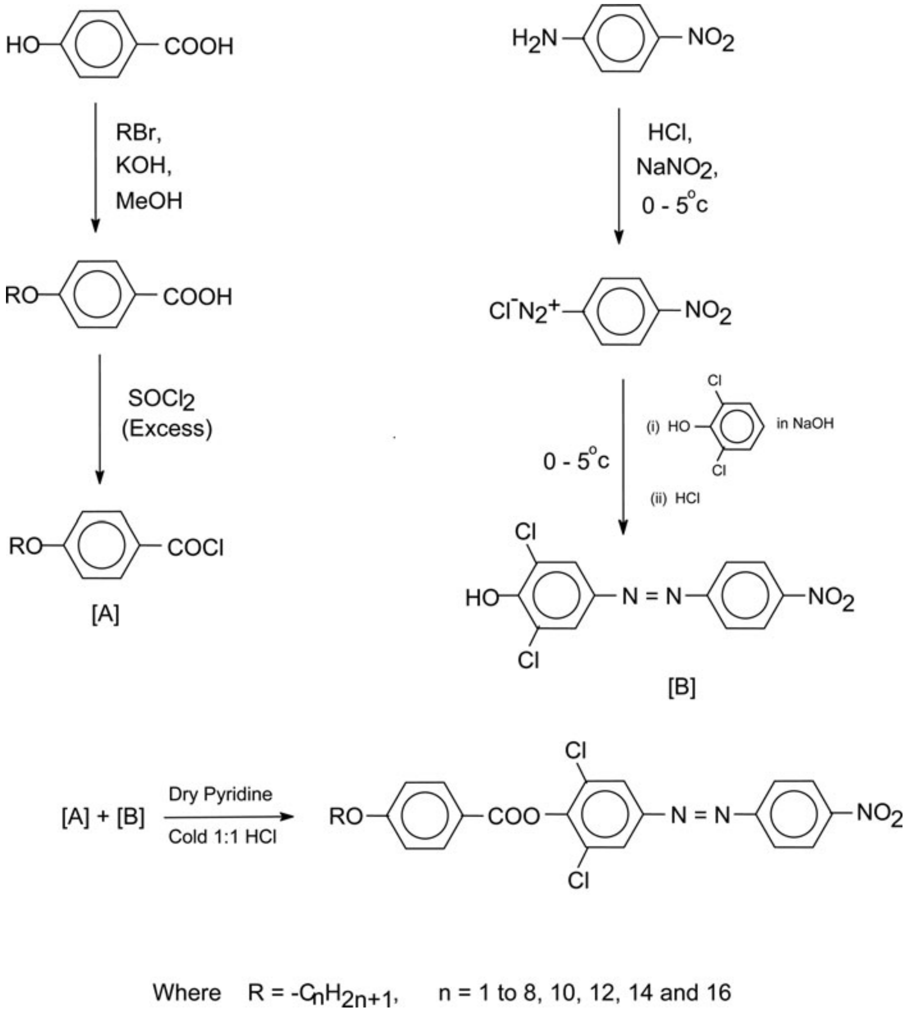
Experimental

Synthesis

2,6-dichlorophenol, 4-nitroaniline, sodium nitrite, pyridine, thionyl chloride, 4-hydroxy benzoic acid, and n-alkyl halides were used directly as received. The solvents were dried and distilled before use. The synthetic route to the present series is illustrated in Scheme 1. 4-n-Alkoxy benzoic acid and corresponding 4-n-alkoxy benzoyl chlorides (A) were synthesized by the modified method of Dave and Vora [17]. 4-Hydroxy-3,5-dichlorophenylazo-4′-nitrobenzene (B) was prepared by a known method [18, 19]. 4-(4′-n-Alkoxy benzoyloxy)-3,5-dichloro phenylazo-4″-nitrobenzenes were synthesized by condensing 4-n-alkoxy benzoyl chlorides (A) with 4-hydroxy-3,5-dichlorophenylazo-4′-nitrobenzene (B) in pyridine [20, 21]. Synthetic route to the series is shown in Scheme 1.

Characterization

Some members of the series were characterized by elemental analysis, infrared (ir) spectra, Hydrogen-1 nuclear magnetic resonance (^{1}H-NMR) spectra, mass spectra, and texture determination by a miscibility method. Microanalysis of the representative compounds was performed on a Perkin Elmer PE 2400 CHN analyzer as shown in Table 1. IR spectra were performed on Perkin Elmer spectrometer and ^{1}H-NMR spectra were performed on Bruker spectrometer using $CDCl_3$ as solvent. LC properties were investigated on a Leitz Laborlux 12 POL polarizing microscope with a heating stage.



Scheme 1. Synthetic route to series-1.

Scheme Spectral Data

IR for n-Bulyloxy Derivative (in cm^{-1})

2948, 2856, 1457.1, 1390 (alkyl group), 1733.8, 1239.2 (ester group), 1599 (—N=N— group), 1559.3 (—C=C— aromatic stre.), 1343.3, 1521.7 (Ar-NO2, nitro group), 1164 (ether group), 849.6 (p-sub. benzene ring), 1043.4 (C—Cl aromatic).

IR for n-Dodecyloxy Derivative (in cm^{-1})

2921, 2850.6, 1467.7, 1391.1 (alkyl group), 1739.7, 1243 (ester group), 1602.7 (—N=N— group), 1560.3 (—C=C— aromatic stre.), 1342.4, 1528.5 (Ar-NO2, nitro group), 1163 (ether group), 847.7 (p-sub. benzene ring), 1033.8 (C—Cl aromatic).

Table 2. Transition temperatures (in °C) for 4-(4′-n-alkoxy benzoyloxy)-3,5-dichloro phenylazo-4″-nitro benzenes

Compound No.	n-alkyl group $-C_nH_{2n+1}$ (n)	Sm	N	Isotropic
1	1	—	—	171.0
2	2	—	(100.0)	108.0
3	3	—	(123.0)	133.0
4	4	—	109.0	135.0
5	5	—	98.0	119.0
6	6	—	(130.0)	132.0
7	7	—	(114.0)	126.0
8	8	—	(118.0)	128.0
9	10	—	63.0	98.0
10	12	—	68.0	101.0
11	14	—	—	123.0
12	16	—	—	170.0

Notes. Sm: smectic, N: nematic.
Values given in parentheses indicate monotropy.

^{1}H-NMR in $CDCl_3$, δppm for n-Heptyloxy Derivative

0.9 (t, 3H, $-CH_3$), 1.33–1.55 (m, 8H, 4x-CH_2-), 1.84 (m, 2H, $-OCH_2$-$\underline{CH_2}$-), 4.07 (t, 2H, $-O\underline{C}H_2$-), 7.0–8.39 (d, 8H, Ar-H), 8.05 (s, 2H, Ar-H).

^{1}H-NMR in $CDCl_3$, δppm for n-Octyloxy Derivative

0.89 (t, 3H, $-CH_3$), 1.31–1.47 (m, 10H, 5x$-CH_2$-), 1.83 (m, 2H, $-OCH_2$-$\underline{CH_2}$-), 4.06 (t, 2H, $-O\underline{CH_2}$-), 6.99–8.43 (d, 8H, Ar-H), 8.05 (s, 2H, Ar-H).

Mass Spectra for Pentyloxy Homologue

Theoretical (calculated) = 502
Experimental = 502

Textures of Nematic Phase by Miscibility Method

Butyloxy homologue = threaded.
Decyloxy homologue = schlieren.
Dodecyloxy homologue = schlieren.

Results and Discussion

A novel LC homologous series of azoesters comprising 12 members has been synthesized and evaluated. Nine members exhibit nematogenic LC property, and only three are not LC. The ethoxy, propyloxy, hexyloxy, heptyloxy, and octyloxy homologues are monotropic nematic and the rest of the LC homologues are enantiotropic nematic. Transition temperatures (Table 2) of novel homologues were plotted versus the number of carbon atoms present in the n-alkoxy terminal end group. Transition curves were drawn by linking similar or related

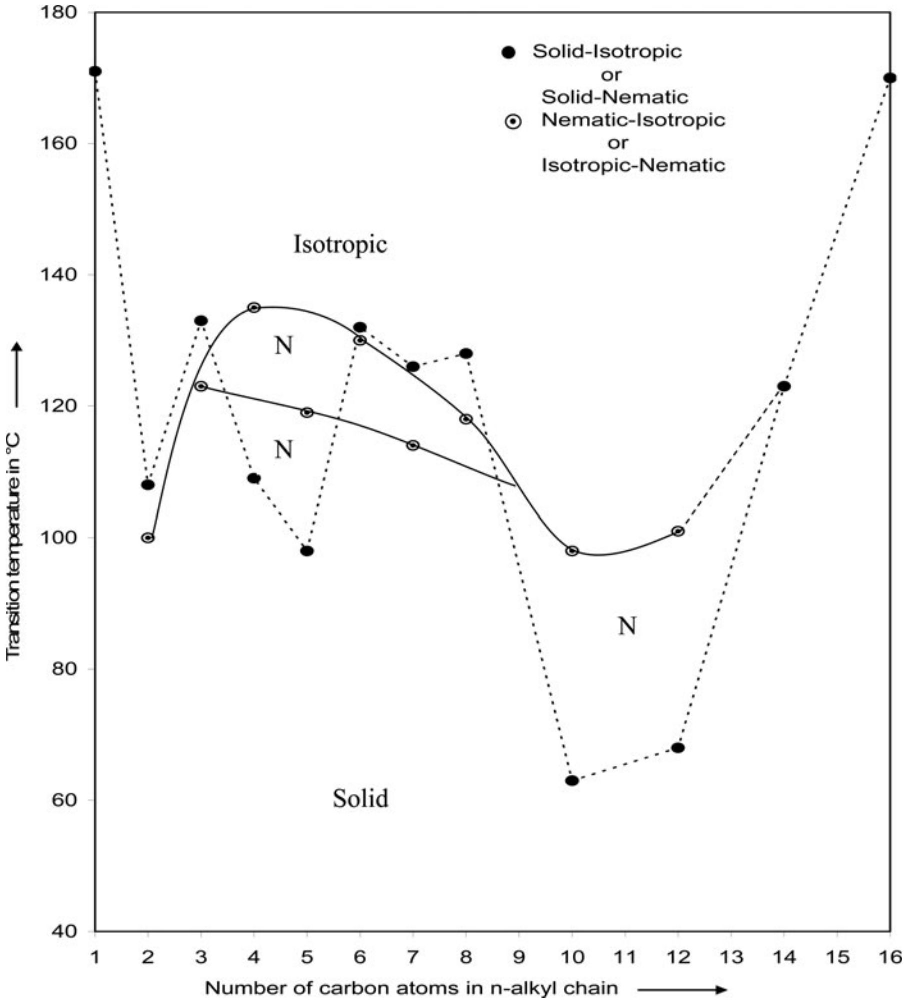


Figure 1. Phase behaviors of a series.

points, constituting a phase diagram (Fig. 1), which shows phase behavior of the series. The solid–isotropic/nematic transition curve follows a zigzag path of rising and falling values with a descending tendency up to the dodecyloxy LC homologue derivative. The N-I transition curve initially rises smoothly, passes through maxima at butyloxy (C_4) homologue, and then descended to dodecyloxy (C_{12}) homologue with an overall descending tendency. The N-I transition curve exhibits an odd-even effect. The N-I transition curve is extrapolated [22–24] to C_{14} homologue to predict its nematic transition temperature, following the trend of N-I transition curve. The transition curves for odd and even members merge into each other at the nonyloxy homologue. The series under discussion is predominantly nematogenic with the absence of smectogenic character, and is of a middle-ordered melting type.

Nine members of the novel series (C_2 to C_8, C_{10}, and C_{12}) out of 12 members exhibited nematogenic mesomorphism in either monotropic (C_2,C_3,C_6,C_7,C_8) manner or enantiotropic (C_4, C_5, C_{10}, C_{12}) manner. Molecules of C_1, C_{14}, and C_{16} homologues are

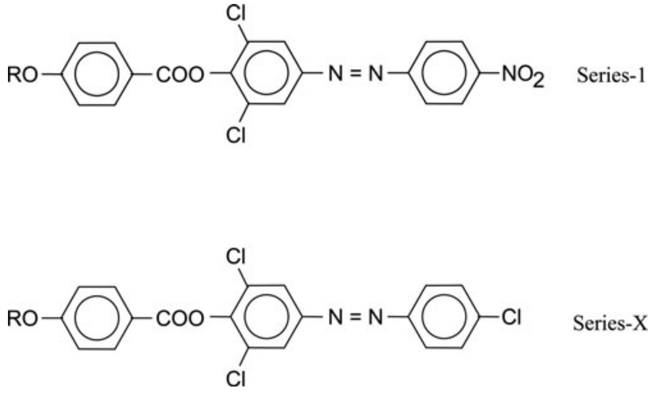


Figure 2. Structurally similar series.

unable to withstand exposed thermal energy due to inadequate and unsuitable magnitudes of anisotropic forces of end-to-end and lateral attractions, as a consequence of unfavorable molecular rigidity and flexibility from their molecular structure. Some molecules (monotropic), on cooling the isotropic melt, develop suitable magnitudes of anisotropic forces of intermolecular attractions and show mesophase formation below the isotropic temperature for a short range of temperatures, depending upon the rate of cooling of melt. Thus, substances showing mesophase only below isotropic temperature in (i) irreversible manner are monotropic LC, or in (ii) reversible manner, i.e. on heating and cooling, are enantiotropic LC, or in (iii) neither reversibly nor irreversibly manner, i.e. does not show LC phase, are NLC. The molecules which exhibit mesophase formation are disaligned at an angle less than 90° with the plane of a floating surface with statistically parallel orientational order to exhibit nematic mesophase. The nematogenic and non-mesogenic homologues of present series bear absence of lamellar packing of molecules in their crystal lattices due to unsuitable magnitudes of the extent of molecular noncoplanarity, which hinders the formation of smectogenic mesophase. The diminishing of odd-even effect beyond merging of curves for odd and even effect for higher homologues is attributed to the coiling or bending or flexing, or coupling of n-alkyl chain with the principal axis of the core structure of a molecule. Variations in LC behavior from homologue to homologue in the present series are attributed to the sequentially added methylene unit at the n-alkoxy chain bonded with a phenyl ring. Average thermal stability for nematic calculated on the basis of enantiotropic homologues (C_4, C_5, C_{10}, and C_{12}) is relatively low, but the energies stored by the respective homologue (ΔH) molecules are sufficient to facilitate and stabilize nematic mesophase formation.

Extrapolation [25, 26] of N-I transition curve merges into the solid–isotropic transition temperature, which indicates that the predicted N-I transition temperature of C_{14} and solid–isotropic transition temperature are the same. Therefore, the molecules of C_{14} do randomly orient from and beyond its isotropic temperature. Thus, there is no possibility of nematic mesophase formation for C_{14} and C_{16} homologues due to unfavorable magnitudes of anisotropic forces of intermolecular end-to-end attractions as a consequence of unsuitable magnitudes of molecular rigidity and molecular flexibility.

The LC behaviors of the presently investigated series-1 are compared with the structurally similar known homologous series-X [27] as shown in Fig. 2.

The presently investigated homologous series-1 and a structurally similar homologous series-X chosen for comparison are identical in all respects except for the right-sided terminal end groups of $-NO_2$ and $-Cl$. The phenyl rings are bridged by $-COO-$ and $-N{=}N-$ central groups contributing mainly to the molecular rigidity, and a varying terminal end group –OR for the same homologue from series to series, which contributes some part to the total molecular flexibility. The changing parts of the same homologue from series to series are $-NO_2$ and $-Cl$ substituted at the para position of $-N{=}N-$ central bridges, which cause variations in total molecular rigidity and flexibility (including common share by too laterally substituted $-Cl$ group) of both the series under comparison. Thus, variations observed in LC behavior and the degree of mesomorphism from homologue to homologue in the same series and from series to series for the same homologue are attributed to the changing molecular rigidity and flexibility. Table 3 represents some LC behavior of series-1 and the known series-X chosen for comparison.

Table 3 indicates the following:

- Series-1 and series-X under comparison consist of 12 homologues, with nine and six members respectively showing enantiotropically or monotropically nematogenic behavior without exhibition of a smectogenic mesophase.
- Only N-I thermal stabilities are calculated on the basis of enantiotropic transition temperatures of C_4, C_5, C_{10}, and C_{12} homologues for series-1, but N-I and I-N thermal stability together is calculated for series-X.
- Mesophase length (nematic) is presented on the basis of enantiotropic transition temperatures only.
- Mesophase formation commences from C_2 and C_4 for series-1 and series-X respectively.
- Series-1 and series-X are predominantly monotropic nematic and partly enantiotropic nematic with low degree of mesomorphism.

The laterally substituted dichloro group in the middle phenyl ring broadens the molecules. As a result, on one hand the intermolecular distance increases and intermolecular end-to-end attraction reduces. On other hand, the molecular polarizability due to lateral substitution increases and the intermolecular attractions increase. Thus, two opposing effects are operating at the same time in both series-1 and series-X. Early or late commencement of the mesophase depends upon the extent of noncoplanarity of molecules. The $-NO_2$ terminal end group is triatomic and $-Cl$ end group is monoatomic, with different group polarity yields different values of the extent of noncoplanarity of a molecule. Thus, the nematic mesophase commences from C_2 homologue in the present series but it commences late from the C_4 homologue of series-X.

Table 3. Average thermal stability (in °C)

Series	1	X
Nematic–isotropic or Isotropic–nematic	113.25 (C_4-C12)	96.3 (C_4-C10)
Commencement of nematic phase	C_2	C_4
Mesophase length range	21°C to 35°C	21°C

Conclusions

- Azoester novel series of 12 homologues exhibits monotropic or enantiotropic mesomorphism of nematic type without exhibition of any smectic property by nine members of the series.
- Mesomorphism induced by favorable magnitudes of molecular flexibility emerged by para substituted $-NO_2$ or $-Cl$ terminal end group or tail group.
- Group efficiency order derived on the basis of (i) thermal stability and (ii) early commencement of mesophase (N) are as follows:
  (i) Nematic: $-NO_2 > -Cl$
  (ii) Nematic: $-NO_2 > -Cl$
- Molecular rigidity and flexibility are very sensitive and susceptible to molecular structure.
- Favorable molecular rigidity and flexibility of suitable magnitudes, which induce LC behaviors in a substance, depend upon the status of n-alkyl chain bonded to phenyl ring through oxygen atom.
- The phenomena of mesomorphism is related to the molecular shape, size, aromaticity, polarity and polarizability, dispersion forces, position of substitution of the same or different functional group or groups, etc., i.e. molecular structure is effective to mesomorphism.

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References

[1] Reinitzer, F. (1888). *Monatsch*, *9*, 421.
[2] Gray, G. W. (Ed.) (1958). In: *Steric Effects in Conjugated Systems*, p. 160, Butterworths: London.
[3] Gray, G. W., & Jones, B. (1954). Mesomorphism and chemical constitution, Part-I, the n-alkoxy naphthoic acids, *J. Chem. Soc.*, 683–686.
[4] Demus, D. (1988). *Mol. Cryst. Liq.Cryst.*, *165*, 45–84.
[5] Demus, D. (1989). *Liq. Cryst.*, *5*, 75–110.
[6] Imrie, C. T., & Taylor, L. (1989). *Liq. Cryst.*, *6*, 1.
[7] Gray, G. W. (1962). *Molecular Structure and Properties of Liquid Crystals*, Academic Press: London.
[8] Gray, G. W., & Winsor, P. A. (1974). *Liquid Crystals and Plastic Crystals*, Vol. 1, Chapters 4 & 7, Ellis Harwood: Chichester, UK.
[9] Gray, G. W., & Jones, B. (1954). Mesomorphism & chemical constitution, Part-3, the effect of halogen substitution on the mesomorphism of the 4-alkoxy benzoic acids, *J. Chem. Soc.*, 2556–2562.
[10] Gray, G. W. (1979). *Liquid Crystals and Molecular Structure in Molecular Physics*, pp. 1–30, Academic Press: London.
[11] Shah, N. H., Vora, R. A., & Jadav, N. D. (1991). *Mol. Cryst. Liq. Cryst.*, *209*, 291.
[12] Nagaveni, N. G., & Prashad, V. (2013). *Phase Trans.*, *86*(12), 1227–1240.
[13] Hird, M., Toyne, K. J., & Gray G. W. (1993). *Liq. Cryst.*, *14*, 741.
[14] Hird, M., Toyne, K. J., Gray G. W., Dok, S. E., & Mc. Donnell, D. G. (1993). *Liq. Cryst.*, *15*, 123.

[15] Gonzalez, Y., Ros, M. B., Serrano, J. L., & Pereziubind, A. (1998). *Liq. Cryst.*, *18*, 751.

[16] (a) Marcos, M., Omenat, A., Serrano, J. L., & Ezcurra, (1992). *Adv. Mater*, 4, 285. (b) Collings, P. J., & Hird, M. (1997). *Introduction to Liquid Crystals Chemistry and Physics*, Taylor and Francis: New York.

[17] Dave, J. S., & Vora, R. A. (1970). *Liquid Crystal and Ordered Fluids*, J. F. Johnson & R. S. Porter (Eds.), Plennum Press: New York.

[18] Vogel, A. I. (1989). *Textbook of Practical Organic Chemistry,* 5th ed., 946 pp., ELBS, Longman: London.

[19] Furnish, B. S., Hannford, A. J., Smith, P. G. W., & Tatchelll, A. R. (1989). *Vogel's Text Book of Practical Organic Chem,* 4th ed., Longman: Singapore.

[20] Patel, V. R., & Doshi, A. V. (2010). *Der Pharma Chemica*, *2*(6), 429.

[21] (a) Doshi, A. V., & Makwana, N. G. (2011). *Mol. Cryst. Liq. Cryst.*, *548*, 220. (b) Ganatra, K. J., & Doshi, A. V. (1999). *Proc. Ind. Acad. Sci. (Chem. Sci.)*, *4*(11), 562. (c) Chauhan, B. C., & Doshi, A. V. (2011). *Der Pharma Chemica*, *3*(1), 172.

[22] Tarvadi, J. J., Bhoya, U. C., & Doshi, A. V. (2012). *Mol. Cryst. Liq. Cryst.*, *552*, 10–15.

[23] Lohar, J. M., & Doshi, A. V. (1993). *Proc. Ind. Acad. Sci. (Chem. Sci.)*, *105*, 209–214.

[24] Bhoya, U. C., Vyas, N. N., & Doshi, A. V. (2012). *Mol. Cryst. Liq. Cryst.*, *552*, 104–110.

[25] Doshi, A. V., & Ganatra, K. J. (2000). *J. Ind. Chem. Soc.*, *77*, 61–64.

[26] Joshi, N. N., & Doshi, A. V. (1993). *J. Ind. Chem. Soc.*, *70*, 807–809.

[27] Makwana, N. G., & Doshi, A. V. (2011). *Der Pharma Chemica*, *3*(1), 580–587.